
Methods for Joint Determination of the Surface Tension Coefficient of a Liquid and the Contact Angle of Wetting the Hard Surface

Konstantin Ludanov

Institute for Renewable Energy, NAS of Ukraine, Kiev, Ukraine

Email address:

k.i.ludanov@ukr.net

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Abstract: This article is devoted to the development of fundamentally new methods for the experimental determination of the physical properties of substances - methods of their "joint determination", when not a single property is measured, but two physical properties connected with each other. For example, this is the coefficient of surface tension σ of the liquid and the contact angle θ of wetting the surface by it, which here act as parameters of capillary forces at the interface. The purpose of such methods is not so much a banal arithmetic increase in the obtained experimental data, as a significant increase in their determination accuracy by reducing the statistical error (variance). In such cases, we have the so-called methods of indirect (indirect) measurement, which in this case are based not on the measurement of σ and θ directly, but on the measurement of the height h and weight ΔW of the meniscus hanging on a vertical surface, and on the subsequent solution of the resulting system of two equations that are analytical expressions for h and ΔW (i.e., a system of two equations with two unknowns: σ and θ). In the case of using a Wilhelmy plate in the experiment, the solution of such a system of equations leads to explicit analytical expressions for both unknowns (σ and θ), and in the case of using a cylindrical filament in the experiment, analytical expressions for the unknowns are obtained in an implicit form: in this case, to determine the value of the boundary of the angle θ , a recursive formula is proposed.

Keywords: Surface Tension Coefficient, Contact Angle, Capillary Meniscus, Wilhelmy Plate Method, Newman's Variant, Meniscus Weight, Meniscus Height, Microscope-Cathetometer

1. Introduction

Knowledge of the physical properties of substances (both in liquid and solid phases) is very important for science and technology, without this information new technologies cannot be developed. Therefore, the development of new methods for their determination is very important. Especially when it comes to the development of methods for the complex determination of physical properties, as a result of the implementation of which not one, but several properties are determined at once [1, 2]. Because it is known from the theory of experiment planning [3] that the statistical error of its results (variance) in this case is much lower than in the methods of direct measurements. This is especially important if the methods of individual measurements used in the joint determination method have high accuracy. It is to the

complex methods of determination that the methods of joint determination (more precisely, the methods of the so-called "indirect measurement") of physical properties: the surface tension coefficient and the contact angle (σ and θ), which are presented in this work, belong.

2. Literature Review

At present, many methods are known for the separate determination of the surface tension coefficient σ and, separately, for the contact angle θ . The most famous method for determining σ is the "capillary method" [4], the author of which is J. Jurin (1717). The Wilhelmy plate method (1863) is also widely known [5]. Several other static "drop" methods are used (lying, sitting, hanging, etc.). There are also many dynamic methods for determining the surface tension of a liquid: the Du Nuy method (ring detachment), methods for

counting drops and maximum pressure in a bubble, a jet oscillation method, as well as wave methods (standing and traveling), etc. Quite a few methods are also known, determining the contact angle [6].

Also known [7] and the method of joint determination of the coefficient of surface tension σ and contact angle θ (the so-called "drop and bubble method"), which is carried out in the form of two experiments. In one of them, the height H of the "large drop" lying on a horizontal plate made of the test material is measured, and in the other, the height D of the "large bubble", which is located under the horizontal plate (made of the same material), lying on the surface of the liquid. The unknowns (σ and θ) in it are found by the formulas:

$$\sigma = (D^2 + H^2) \cdot \Delta\rho \cdot g / 4, \text{ (N/m)} \quad (1)$$

$$\cos\theta = (D^2 - H^2) / (D^2 + H^2), \quad (2)$$

where $\Delta\rho$ – is the difference between the densities of liquid and gas, $\Delta\rho = \rho_l - \rho_g$ (kg/m^3), g – acceleration of gravity (m/s^2).

These expressions are obtained by solving a system of two equations with two unknowns (σ and θ), the first of which:

$$\sigma \cdot (1 - \cos\theta) = \Delta\rho \cdot g \cdot H^2 / 2, \quad (3)$$

represents the balance of capillary forces on the contact line of three phases for a "large drop", which lies on a horizontal plate made of the material under study, and the second:

$$\sigma \cdot (1 + \cos\theta) = \Delta\rho \cdot g \cdot D^2 / 2, \quad (4)$$

represents the balance of capillary forces on the contact line of the three phases for the "big bubble", which is located under the horizontal plate of the test material.

However, it turned out that the accuracy of determining the required parameters (σ and θ) of capillary forces at the interface by this method is very low, since it is difficult to provide equilibrium conditions in it during the creation of both a bubble and a drop, that is, both during the inflow and runoff of the liquid. Therefore, the contact angle here is nonequilibrium: moreover, for a drop it is close to the maximum angle of incidence, and for a bubble - to the minimum angle of flow [8].

3. Formulation of the Problem

Obviously, to create new more accurate methods for determining the parameters of capillary forces at the interface (σ and θ), it is necessary to find new ways of their joint determination. And as a basis for such methods, it is necessary to use the most accurate methods of their separate determination.

One of the most accurate methods for a separate determination of the surface tension coefficient σ is the Wilhelmy plate method, the author's version of which is carried out in the form of a single experiment to "weigh" the meniscus hanging on a vertical plate of platinum foil, because for it $\theta = 0$ and $\cos\theta = 1$:

$$\sigma = \Delta W / (p \cdot \cos\theta) = \Delta W / p, \quad (5)$$

where ΔW – is the "weight" of the meniscus (H), p – is the perimeter of the plate (m), θ – is the contact angle (rad. or deg.).

There is another version of the Wilhelmy plate method (the so-called Newman version [9]), which is used to measure the contact angle θ and which differs from the author's version only in that instead of weighing the meniscus, the height is measured using a microscope-cathetometer, the edges of the meniscus h above the surface of the liquid, and the contact angle θ is determined by the formula:

$$\sin\theta = 1 - (h/a)^2, \quad (6)$$

where a – is the "capillary constant" of the liquid, its square: $a^2 = 2\sigma / \Delta\rho \cdot g$ (m^2).

It is known [4] that the error of the author's version of the Wilhelmy plate method is 0.1%, and the error of the "Newman's version" is 0.1 deg. Thus, both of these options are highly accurate; therefore, the creation of a method for joint determination of σ and θ based on these versions of the Wilhelmy plate is very promising, since it will allow creating a method of precision accuracy and, in particular, excluding the use of platinum foil in the installation.

4. Results of Research

4.1. Method for Joint Determination of Capillary Forces Parameters (σ , θ) Based on "Wilhelmy Plate Methods"

On 3.08.2004, the author registered an application for an invention "A method for joint determination of the parameters of capillary forces at the interface" [10], which makes it possible to determine at once two parameters of capillary forces (σ and θ) in a single experiment using a "Wilhelmy plate".

To measure these parameters, we used the Newman-Tanner setup [11] equipped with an electronic balance and a cathetometer microscope. As a result of the experiment, the meniscus hanging on a plate of material with an unknown contact angle θ is simultaneously weighed and, in addition, the meniscus height h is measured with a microscope-cathetometer.

As a result of carrying out a single experiment on a pilot plant, we obtain two equations with two unknowns:

$$\begin{cases} \cos\theta = \Delta W / (\sigma \cdot p) \\ \sin\theta = 1 - \Delta\rho \cdot gh^2 / (2\sigma) \end{cases} \quad (7)$$

This system of two equations with two unknowns has a solution, which, for example, for σ can be easily obtained, for example, using the "basic identity" of trigonometry: $\sin^2\theta + \cos^2\theta = 1$. The obtained solution can be represented in explicit form for both σ and θ :

$$\sigma = (\Delta W / p)^2 / (\Delta\rho \cdot gh^2) + (\Delta\rho \cdot gh^2) / 4 \quad (8)$$

$$\sin\theta = [4(\Delta W / p)^2 - (\Delta\rho \cdot gh^2)^2] / [4(\Delta W / p)^2 + (\Delta\rho \cdot gh^2)^2] \quad (9)$$

Thus, in the new method, firstly, the experiment on weighing the meniscus on a plate of platinum foil is excluded, and secondly, both measurements are carried out simultaneously in a single experiment, which provides a significant simplification of the method and clarification of the procedure for the experimental determination of the parameters σ and θ .

4.2. Method for Joint Determination of Capillary Force Parameters (σ and θ) Based on the "Filament Method"

On June 15, 2006, the author registered an application for an invention "A method for joint determination of the parameters of capillary forces at the interface between phases" [12], which makes it possible to determine at once two parameters of capillary forces (σ and θ) also in a single experiment using the "filament method".

To measure these parameters, a Newman-Tanner setup was also used, equipped with an electronic balance and a cathetometer microscope. Within the framework of one experiment, the meniscus hanging on a plate of material with an unknown contact angle θ is simultaneously weighed and, in addition, the meniscus height h is measured.

The following expression is known for the height of the meniscus edge hanging on the filament [13]:

$$h = R \cdot \cos\theta \cdot \{1 + \ln[(a\sqrt{2})/(1 + \sin\theta) \cdot R]\}^{-1}, \quad (10)$$

where R – is the radius of the filament (m), a – is the capillary constant (m), $a^2 = 2\sigma/\Delta\rho g$ (m²).

And for the weight of the meniscus, you can use the already known expression:

$$\Delta W = \sigma \cdot p \cdot \cos\theta = \sigma \cdot 2\pi R \cdot \cos\theta \quad (11)$$

As a result of analyzing equations (10) and (11), we obtain a system of two equations with two unknowns (a and θ):

$$\begin{cases} \cos\theta = \Delta W / (\sigma \cdot 2\pi R) = \Delta W \cdot \Delta\rho g / (\pi R \cdot a^2) \\ \cos\theta = (h/R) / \{1 + \ln[(a\sqrt{2})/(1 + \sin\theta) \cdot R]\} \end{cases} \quad (12)$$

At first glance, for solving the system of equations (12), it is obvious that the left-hand sides of both equations are equated. However, this will lead nowhere, since in this case we obtain an implicit equation for the unknown a , about which little is known a priori. Therefore, it is better, firstly, by substituting the expression a from the first equation into the second to obtain an implicit expression for $\sin\theta$ and $\cos\theta$, about which it is known a priori that for a lyophilic pair "liquid-filament material" the contact angle θ is very small, $\sin\theta \rightarrow 0$, and $\cos\theta \rightarrow 1$. Therefore, firstly, it is better to express the capillary constant from the first equation of the system and substitute it into the second equation, which is also implicit. But it is quite possible to solve it by the method of "successive approximations" and obtain the value of the unknown contact angle θ .

The expression for the "capillary constant" from equation (12) is as follows:

$$a = \sqrt{[\Delta W / (\pi R \cdot \Delta\rho g \cdot \cos\theta)]} \quad (13)$$

We substitute it into formula (13) and we also obtain an implicit expression for the contact angle θ :

$$\cos\theta = (h/R) / \{1 + \ln[\sqrt{(2\Delta W / (\pi R^3 \cdot \Delta\rho g \cdot \cos\theta))} / (1 + \sin\theta)]\} \quad (14)$$

Analysis of the obtained expression shows that it is impossible to express explicitly a contact angle θ or function $\cos\theta$ from formula (14). Therefore, to calculate it, the author used the method of "successive approximations" [14]. For this, formula (14) must be written in the following form:

$$\theta_{i+1} = \arccos\left\{ \frac{(h/R)}{\{1 + \ln[\sqrt{(2\Delta W / (\pi R^3 \Delta\rho g \cos\theta_i))} / (1 + \sin\theta_i)]\}} \right\} \quad (15)$$

Thus, if, as a result of a single experiment, the meniscus ΔW hanging on the thread is weighed and the height of its edge h above the liquid surface is measured, then it becomes possible to calculate the value of the contact angle θ using the recurrent formula (15) as a result of several iterations. Usually $\theta_1 = 0$ is taken as the first approximation. But if it is possible to photograph the meniscus, then as the first approximation, a more accurate value for $\theta_{i=1}$ from the photograph of the meniscus profile can be used.

After calculating the value of the contact angle θ of wetting the surface of the thread by the liquid according to formula (11), it is easy to establish the second unknown, the coefficient of surface tension:

$$\sigma = \Delta W / (2\pi R \cdot \cos\theta) \quad (16)$$

5. Findings

So, the article presents two very accurate methods of joint determination of the surface tension coefficient of a liquid and the contact angle of wetting the surface under study (plate or thread).

Since both of these parameters of capillary forces are determined simultaneously in a single experiment, then the possibility of errors due to the difference in operating factors even in two experiments is completely excluded, if these parameters were determined separately.

In addition, the joint determination of both parameters can significantly reduce the statistical error of the "indirect measurement", which makes the patented methods highly accurate.

For the installation based on the use of the Wilhelmy plate, the use of a platinum foil plate is excluded, which simplifies the experimental procedure.

And finally, the possibility of determining both parameters in a single experiment makes it possible to use this method not only under stationary conditions, but also in a non-stationary mode (with a continuous change in the phase temperature, solution concentration, gas composition, etc.), i.e. makes it possible to use them as elements of technological installations and technical devices.

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